(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
20 September 2001 (20.09.2001)

PCT

(10) International Publication Number
WO 01/69612 A2

(51) International Patent Classification⁷: H01F 1/00

(21) International Application Number: PCT/IB01/00659

(22) International Filing Date: 13 March 2001 (13.03.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
2000-068579 13 March 2000 (13.03.2000) JP

(71) Applicant (*for all designated States except US*): **SANEI KASEI CO., LIMITED** [JP/JP]; 3-1-8, Nihonbashi, Chuo-Ku, Tokyo (JP).

(72) Inventors; and

(75) Inventors/Applicants (*for US only*): **SEKINE, Shigenobu** [JP/JP]; 2-19-9 Higasi Tateisi Katushika-ku, Tokyo (JP). **NARITA, Minoru** [JP/JP]; 5-15-13 Nisiarai Adathi-ku, Tokyo (JP). **SATO, Hiroji** [JP/JP]; 5-7-4 Ropongi Minato-ku, Tokyo (JP).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:
— *without international search report and to be republished upon receipt of that report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: STRUCTURE OF CRUDE PELLET FOR PLASTIC MAGNET

(57) Abstract: A pellet starting material for the production for a plastic magnet comprising thermoplastic resin having uniformly dispersed therein, a ferromagnetic alloy powder comprised of an aggregate of fine ferromagnetic alloy particles having a nano-composite structure, wherein the nano-composite structure, the fine ferromagnetic particles are isolated with layers or specks of a compound selected from the group consisting of metal oxides, metal nitrides and metal hydrides, or with open spaces, and the ferromagnetic alloy powder grains are spherical.

WO 01/69612 A2

STRUCTURE OF CRUDE PELLET FOR PLASTIC MAGNET

FIELD OF THE INVENTION

This invention concerns the structure and composition of crude pellets used for the production of a plastic magnet.

BACKGROUND OF THE INVENTION

A plastic magnet is produced by the method in which ferromagnetic alloy powder and thermoplastic resin are melted, kneaded, and extruded to form pellets and then the pellets are annealed and reformed in a proper mold under a magnetic field. The composition and the internal structure of the ferromagnetic alloy powder influence the magnetic properties, and the shape influences the forming of the pellets and the plastic magnets.

The ferromagnetic alloy powder is usually produced with mechanical pulverization of an alloy having the proper composition. For example, a powder of the rare earth-iron-boron alloy (R-Fe-B where R is rare earth metal) was produced by the method in which the melted alloy was formed to be a film, cooled rapidly, and pulverized mechanically. In this method, microscopic images of the pulverized powder showed that the powder surfaces were rough and flake-like, and the sizes were not uniform. Using such a rough powder, since its flowability was not smooth on the production of pellets, the amount of the resin or the extrusion pressure should have been increased. Moreover, such a rough shape of the powder was not preferable for the magnetic property of the produced plastic magnet.

SUMMARY OF THE INVENTION

The present invention provides the structure and composition of a crude pellet used for the production of a plastic magnet with excellent magnetic properties.

In this invention, the crude pellet for the plastic magnet has the structure resulting from the melted and kneaded mixture comprising of (1) spherical ferromagnetic alloy powder grains, having a nano-composite structure, is the aggregate of fine particles of the ferromagnetic alloy are isolated respectively with a layer or specks/dots of metal oxides, or with open spaces (pores) and (2) a thermoplastic resin, where the spherical ferromagnetic alloy powder of is uniformly dispersed in the thermoplastic resin. The average diameter of the sphere ferromagnetic alloy powder particles is less than 100 μm, and is preferred to be less than 50 μm.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic drawing of the apparatus used in the method embodying the principles of the present invention;

Figure 2 is a SEM image of the rare earth-iron-boron powder produced with the method of Example 1;

Figure 3 is a high-resolution SEM image of the rare earth-iron boron powder produced with the method of Example 1;

Figure 4 is a SEM image of the pellet produced with the method of Example 1; and

Figure 5 is a SEM image of the pellet produced with the method of Reference 1.

DETAILED DESCRIPTION OF THE INVENTION

First, the spherical ferromagnetic alloy powder with the nano-composite structure used for the magnetic material in this invention and their production method are described. The spherical ferromagnetic alloy powder grains with the nano-composite structure is the aggregate of the fine particles of the ferromagnetic alloy in which the respective fine particles are isolated with the layers or specks/dots of metal oxides, or with open spaces (pores). It is produced by a method in which the melted ferromagnetic alloy is dropped onto a rapidly rotating dish in an atmosphere of argon, oxygen, nitrogen, hydrogen, and/or helium gas, and dispersed to result in small droplets using a centrifugal force, then cooled rapidly in the atmosphere to enable the nano-composite structure self-assembly to occur.

Figure 1 shows an example of the centrifugal granulation apparatus used in the production of the spherical ferromagnetic alloy powder with the nano-composite structure. With respect to the granulation chamber 1, the shape of the upper part is a cylinder and that of the lower part is a cone. There is a lid 2 on the granulation chamber 1. At the center of the lid 2, a nozzle 3 is inserted perpendicularly. Under the nozzle 3, a rotating dish 4 is set. The line 5 indicates the feedthrough mechanism for the moving of the rotating dish 4 up and down. Under the cone of the granulation chamber 1, an exit tube 6 for the produced powder is connected. The upper part of the nozzle 3 is connected with an electric oven (e.g., microwave oven) 7 for the melting of the granulating ferromagnetic alloy. In the gas tank 8, the atmosphere gas whose component is controlled, transits tubes 9 and 10 and is supplied to the granulation chamber 1 and the electric oven 7. The pressure in the granulation chamber 1 is controlled with a valve 11 and a vacuum pump 12. The pressure in the electric oven 7 is controlled with a valve 13 and a vacuum pump 14.

When the pressure in the electric oven 7 is set a little bit higher than the atmospheric pressure and the pressure in the granulation chamber 1 is set a little bit lower than the atmospheric pressure, the melted metals in the electric oven 7 are dropped from the nozzle 3 to the rotating dish 4 due to the difference of the pressures. The dropped metals are dispersed to be small droplets due to the centrifugal force of the rotating dish 4, and are cooled down to be solid powder. The produced powder is ejected from the tube 6 through an automatic filter 15 and is fractionated. The sign 16 indicates a collection chamber of the powder.

If the shape of the rotating disk is a disk or a cone, it is difficult to obtain the desired size powder since the centrifugal force on the metal droplets depends on the dropped position of the rotating target. When the shape of the rotating target is a dish, the dependence of the centrifugal force on the metal droplets on the dropped position is small. Due to the uniform centrifugal force existing at surrounding positions of the dish, specifically sized droplets are dispersed. These dispersed droplets were then cooled rapidly, solidified and dropped for collection.

The inventors studied the granulation of the melted ferromagnetic alloy using the above apparatus. They found that the melted ferromagnetic alloy was self-assembled (i.e., the alloy automatically formed) on the rapid cooling and became the metal powder with the nano-composite structure in which the respective small particles were isolated with the layers or specks/dots of metal oxides, metal nitrides, and/or metal hydrides, or with the open spaces (pores). The respective small particles were isolated in the same manner as above depending upon the compositions of the starting metals and in the atmosphere of the various gases. The term, "self-assembling" means that the melted metals form the nano-composite structure automatically in the process of dispersing and rapid cooling.

The faster the rotating speed of the dish, the smaller the size of the resulting powder. When a dish with the inner diameter of 35 mm and the depth of 5 mm is used, more than 50000 rpm is preferable in order to obtain the powder with the average size less than 100 μm.

The temperature of the atmosphere gas supplied in the granulation chamber can be room temperature. However, in case of long continual production, the temperature in the granulation chamber should be less than 300° C in order to ensure the rapid cooling of the metal droplets.

A proper resin usually used for the production of the plastic magnet, e.g., nylon, can be used as the thermoplastic resin in this invention.

The following are the references and the examples of the production method and their results. This invention is, however, not restricted in these examples.

REFERENCE 1

To Nylon12 resin at 12 weight% was added the conventional ferromagnetic powder, produced by rapid cooling of the film-shape rare earth-iron-boron alloy (R-Fe-B where R is rare earth metal), at 88 weight%. The mixture was annealed, kneaded, extruded, and cut to be rice-size pellets. The limit of the extrusion using the extruder was less than 90 weight % of the ferromagnetic powder. The pellets were annealed and molded in the magnetic field of 2 Tesla (T), and a cubic 1 cm^3 plastic magnet was obtained. The measured magnetic properties of the plastic magnet are shown in Table 1.

EXAMPLE 1

Using the apparatus shown in Figure 1, the melted rare earth-iron-boron alloy, whose composition was the same as that used in Reference 1, was dropped

onto the rotating dish with the inner diameter of 35 mm and the depth of 5 mm in the argon gas with 500 ppm oxygen. The dispersed droplets were rapidly cooled to be a powder with the average size of 30 μm. To Nylon12 resin at 7 weight % was added the produced powder at 93 weight %. The mixture was annealed, kneaded, extruded, and cut to be rice-size pellets. The limit of extrusion using the extruder was less than 95 weight % of the ferromagnetic powder. The pellets were annealed and molded in the magnetic field of 2 T, and a cubic 1 cm^3 plastic magnet was obtained. The measured magnetic properties of the plastic magnet are shown in Table 1. Figures. 2 and 3 show a scanning electron microscope (SEM) image and its magnified image of the rare earth-iron-boron alloy powder (average size: 30 μm) obtained from the process of Example 1, respectively. From Figure 2, it is confirmed that the shape of the obtained powder is a sphere and the powder has a fine net structure. From Figure 3, it is confirmed that the powder is an aggregate of the fine particles (nano-particles) and each particle is isolated respectively. From another experiments, it is confirmed that the fine particle (main phase) is an R-Fe-B alloy and the isolating layer (black net in the images of Figures 2 and 3) is a rare-earth metal oxide.

Figures 4 and 5 show SEM images of the pellets produced in Example 1 and Reference 1, respectively. From Figure 4, it is found that the size-ordered ferromagnetic powder (sphere shape) is dispersed uniformly in the resin, and the pores (white domains in the SEM image) are little. From Figure 5, it is found that the big and small ferromagnetic powder (flake shape) is dispersed heterogeneously, and the pores (white domains in the SEM image) are large.

TABLE 1

Property	unit	Example 1	Reference 1
Br	G	9382	5346
iHc	Oe	10807	11296
(BH)max	MGOe	17.4	6.4

From Table 1, the plastic magnet produced from the crude pellets with the invented structure (Example 1) has nearly three times higher (BH)max value than the plastic magnet produced from the conventional crude pellets (Reference 1). This result is due to the superior features of the invented crude ferromagnetic powder; having nano-composite structure, little added resin, and having little pores.

Thus, the crude pellets used for the production of the plastic magnet have excellent magnetic properties.

While only a few exemplary embodiments of this invention have been described in detail, those skilled in the art will recognize that there are many possible variations and modifications which may be made in the exemplary embodiments while yet retaining many of the novel and advantageous features of this invention. Accordingly, it is intended that the following claims cover all such modifications and variations.

What is claimed is:

1. Ferromagnetic alloy powder comprised of an aggregate of fine ferromagnetic alloy particles having a nano-composite structure, wherein the nano-composite structure, the fine ferromagnetic particles are isolated with layers or specks of a compound selected from the group consisting of metal oxides, metal nitrides and metal hydrides, or with open spaces, and the ferromagnetic alloy powder grains are spherical.

2. The ferromagnetic alloy powder of claim 1 wherein the ferromagnetic alloy is a rare earth-iron-boron alloy.

3. The ferromagnetic alloy powder of claim 1 wherein the average diameter of the spherical ferromagnetic alloy powder grains is less than 100 μm.

4. The ferromagnetic alloy powder of claim 1 wherein the average diameter of the spherical ferromagnetic alloy powder grains is less than 50 μm.

5. The ferromagnetic alloy powder of claim 1, wherein the fine particles are isolated with layers or specks of metal oxides.

6. A pellet starting material for the production of a plastic magnet comprising thermoplastic resin having uniformly dispersed therein, a ferromagnetic alloy powder comprised of an aggregate of fine ferromagnetic alloy particles having a nano-composite structure, wherein the nano-composite structure, the fine ferromagnetic particles are isolated with layers or specks of a compound selected from the group consisting of metal oxides, metal nitrides and metal hydrides, or with open spaces, and the ferromagnetic alloy powder grains are spherical.

7. The pellet of claim 6, wherein the thermoplastic resin is nylon 12.

Fig. 1:

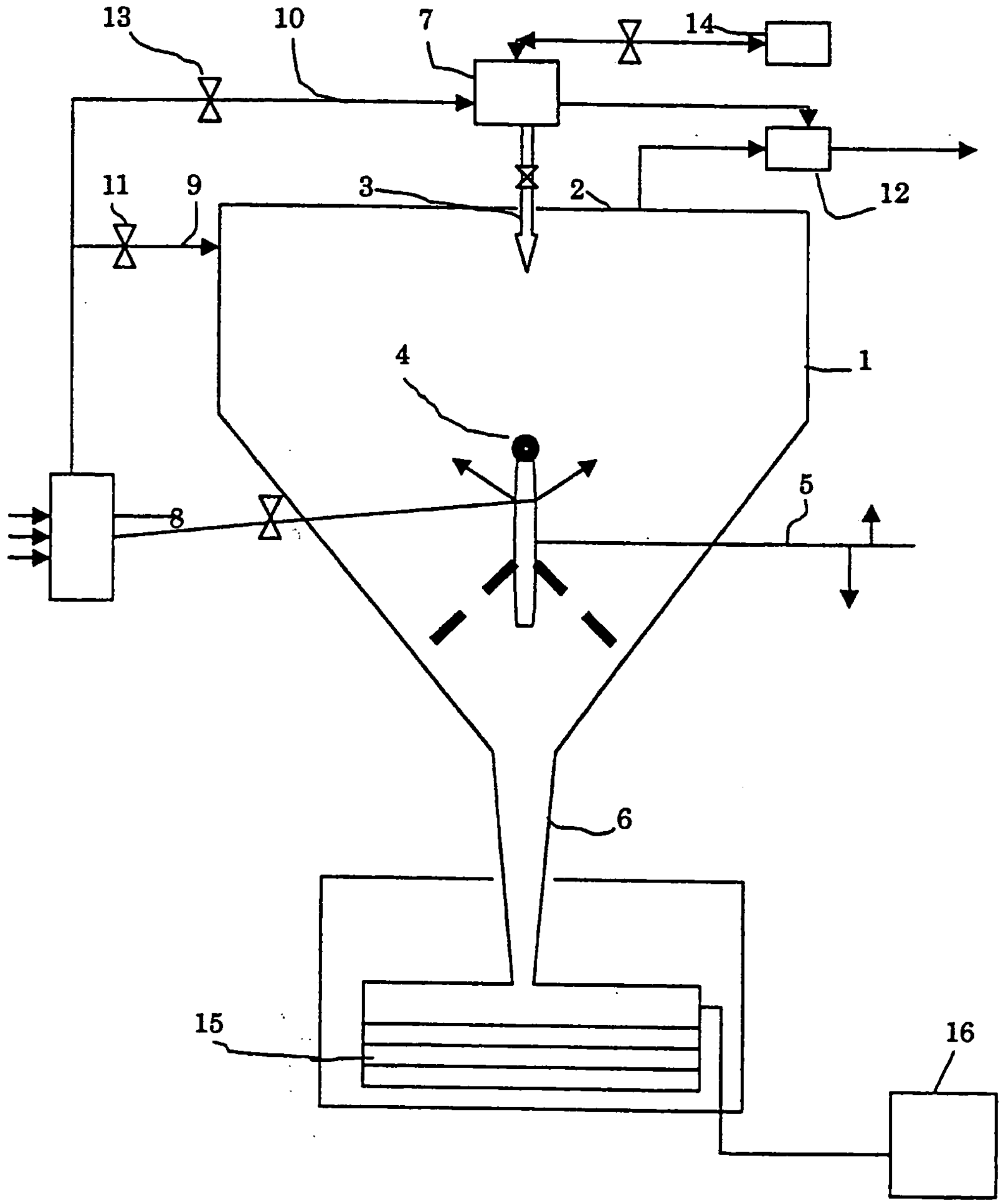
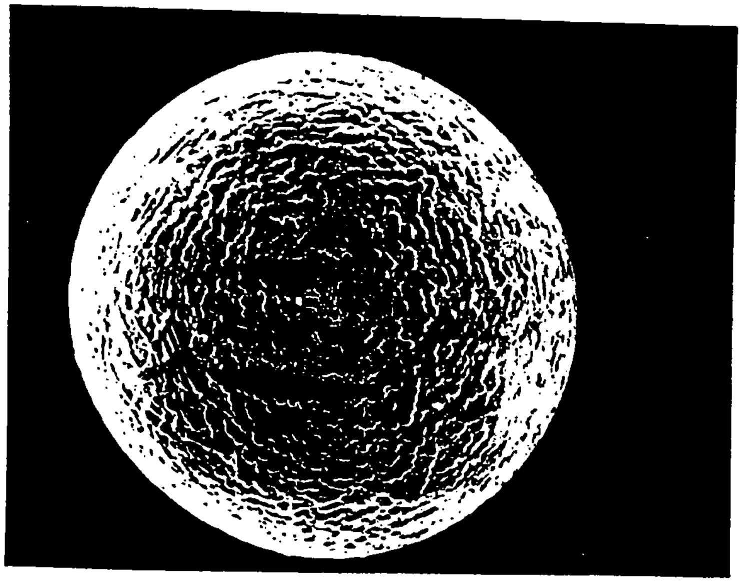


Fig. 2



ROx-R-Fe-B

25.0KV X250 10μm

Fig. 3

ROx-R-Fe-B

25.0KV X600 5μm

Fig. 4:

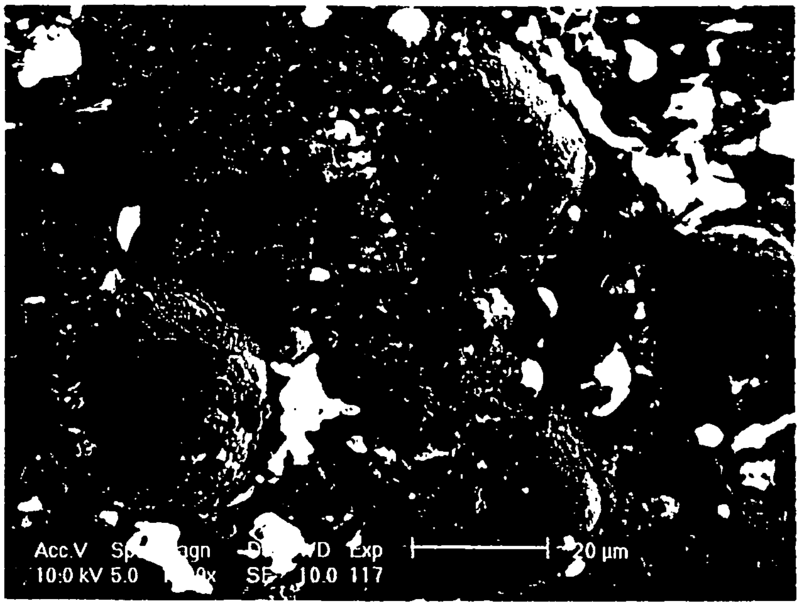


Fig. 5: